Fuel Processing Research and Development - Preferential Oxidation Clean-Up

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Objectives

- Develop automotive-scale gas cleanup technology to convert fuel processor output into PEM fuel cell quality gas.

Approach

- Develop PROX hardware and control systems to support industrial collaborations including those for the ADL/LANL/Plug Power gasoline system demonstration, and the Energy Partners 10kWe PEM system.
- Develop the capability to quantify the transient performance of PROX hardware and control systems at 50kWe equivalent simulated gasoline reformate flows.
- Develop a flexible, easily reconfigured 50-kWe PROX test reactor.
- Develop computer models of steady-state and transient PROX operation for experimental analysis, design and optimization, and control system algorithm development.

2. Investigate catalysts and catalyst configurations for optimum catalyst utilization as well as characterization of current PROX catalysts.
3. Acquire partial oxidation fuel processors for investigating PROX performance with real reformate, effect of fuel impurities, and control system integration.

Accomplishments

- A standalone PROX subsystem was fabricated, tested, and then integrated into the ADL/LANL/Plug Power gasoline-powered PEM fuel cell system demonstration in Cambridge, MA.
- The LANL PROX test facility was redesigned and rebuilt for transient control and measurement capability at 50kWe gasoline reformate flows.

4. A modular 50kWe PROX was designed, fabricated and tested.
5. Experiments were conducted to map the steady-state performance of the 50- kWe PROX and also its transient performance through both flow and CO concentration transients. Control of outlet CO was demonstrated through the transients.

- A steady-state PROX design model was formulated.
- A PROX subsystem has been designed and fabricated for use in the Energy Partners 10kWe PEM fuel cell system.

Future Direction

- Continue parameterization and optimization experiments on 50 kWe PROX to support transient automotive requirements, including startup.
- Install partial oxidation fuel processors for PROX system integration.
- Continue interactions with industrial developers to integrate and test LANL PROX hardware with commercial fuel cell systems.

- Continue catalyst development and optimization for automotive applications.

Introduction

This report describes FY98 technical progress on gas cleanup. These LANL investigations focused on increasing the state-of-the-art of preferential oxidation (PROX) clean-up technology for automotive applications. The main thrust explored PROX hardware at an automotive scale (50 kWe flows) with the design capability to alter outlet CO concentrations to fuel cell quality not only under steady state conditions but also through anticipated transients for an automotive application. PROX operating experience was acquired both in our expanded experimental facility and in collaboration with industrial developers. Our accomplishments in our main tasks are described below.

ADL/LANL/Plug Power Gasoline Fuel Cell Demonstration

A portable PROX subsystem was designed, built and thoroughly tested for use in the demonstration of a gasoline-powered PEM fuel cell system by the team of Arthur D. Little, Inc. (ADL), Plug Power, L.L.C., and Los Alamos National Laboratory. The PROX reactor, shown in Figure 1, was based on a scaled-down version of an entirely novel LANL 50 kWe PROX design. Operating points for the air injection and temperature set points required to maintain outlet CO concentrations below 50 ppm were determined during testing at Los Alamos. Figure 2 illustrates outlet CO concentrations measured during these tests at flows equivalent to 10 kWe and 5 kWe with synthetic gasoline reformate (36% H_2, 28% N_2, 17% CO_2, 17% H_2O) over a range of inlet CO concentrations.

The PROX subsystem was integrated into a portable test fixture controlled with a LabVIEW-based data acquisition and control system, and then shipped to the Cambridge, MA where the LANL PROX test fixture was integrated with the POX and fuel cell components. (This test fixture included another 5-kW fuel cell stack and the necessary components to operate that device. This stack served as a backup to the subject hardware from Plug Power, L. L. C.) Successful system tests were completed with this PROX operating on both gasoline- and ethanol-derived feed streams. This component modified the chemical composition emanating from the ADL POX and with the PROX effluent containing less than 50 ppm and below 20 ppm for significant stretches of the test. Both the Plug Power fuel cell stack and a Ballard MarkV fuel cell stack were operated successfully on feed streams emanating from the PROX.

Figure 3 shows typical data recorded on the PROX outlet CO concentration operating on gasoline reformate. During this time interval, the PROX was operated under steady-state conditions marked by fixed air injection and temperature settings. Transients in the outlet CO concentration were observed at regular intervals, the result of in either inlet CO concentration to the PROX, gas composition, or variations in total flow rate. These observed performance transients must be considered as preliminary data and may or may not be a feature of more advanced fuel processing hardware, such as being developed within the DOE program.

50 kWe Experimental PROX and Test Facility

A 50 kWe modular PROX test reactor was designed, fabricated, and tested. This experimental PROX, shown in Figure 4, is a four unit device including an inlet gas conditioning unit followed by three active catalyst stages. Overall fast transient performance is achieved while reducing overall volume through the use of a regenerative design which incorporates heat exchange, air injection, and mixing. The overall hardware is formed using a modular, flanged design. In this way, catalysts and catalyst configurations can be rapidly modified and details of the integrated heat exchange varied as required. Of course, safety features required for operation with hydrogen feed mixtures are maintained.

Previously, the largest PROX hardware tested at Los Alamos was the 10-kW devices built under DOE sponsorship. Consequently, the laboratory required extensive modification to accommodate the required higher chemical flow rates. The PROX experiment facility was upgraded to generate required simulated reformate flows for a fuel cell power system operating over the range of 10 kWe to 50 kWe output (exported) electric power. Correspondingly, hydrogen chemical flow capacity was increased to a maximum of 140 kWch (based on the LHV) along with the requisite quantities of nitrogen, carbon dioxide, and steam to simulate a "wet gasoline reformate" with sufficient hydrogen to generate 50 kW of electricity for export to traction motors. These modifications required extensive improvements in the data acquisition and control system to provide a transient control capability with competence to vary timing of control parameters and to mimic the composition and time response of transient behavior generated by upstream components. Transient measurement capability was also included by the addition of online gas analyzers for carbon monoxide, methane, and oxygen. These instruments supplement the conventional gas chromatography measurements.

50 kWe PROX Experiments

Experiments were conducted to characterize the steady-state performance of the new 50 kWe PROX, to characterize the transient response of the PROX as changes in flow rate and gas composition occur, and to identify CO control strategies that achieve low CO levels through these transients. The set of experiments reported here were conducted with a synthetic gasoline reformate.

Variables required to map the steady-state performance of the 50 kWe PROX include overall flow rate, inlet CO concentration, inlet temperature, and oxygen flow rates for each of the three stages. Steady-state PROX performance data are shown in Figures 5 through 8. Figures 5 and 6 show the outlet CO and CH_4 concentrations, respectively, as a function of oxygen stoichiometry for stage 1 at a flow rate of 100 kWch gasoline reformate with 8000 ppm CO at the inlet. The graphs illustrate the influence of inlet temperature on the outlet CO concentration and the CH_4 production. Both of these reactions influence the quantity of hydrogen consumed during the cleanup operation.

Figures 7 and 8 show the outlet CO concentration as a function of overall oxygen stoichiometry summed to include all three PROX stages under conditions using a 100 kWch gasoline reformate with 8000 ppm inlet CO. The second stage outlet CO concentrations shown here were obtained with the first stage operating with an oxygen stoichiometry of 1.2. Data for the third stage outlet CO concentrations, detail in Figure 8, were measured with the first and second stages operating at an oxygen stoichiometry of 1.2 and 1.95, respectively. In general, the device performed as designed over a wide range of flow rates and CO inlet concentrations.

Two types of transient experiments with the 50 kWe PROX are described here. The first type measured the outlet CO concentration during a 90 second step increase in the inlet CO concentration from 8000 ppm to 12000 ppm. Before this transient, the PROX settings were maintained optimized for the steady state, 8000 ppm CO concentration. Data are shown in Figure 10 for two cases: 1.) the air injection rates were held steady through the pulse (no control), and 2.) the air injection rates were held proportional to the inlet CO flow (controlled). With no control, the inlet CO pulse resulted in an outlet CO pulse rising from approximately 30 ppm CO to above 1500 ppm CO. However with simple control, the outlet CO concentration appeared constant through the short term CO transient. This experiment illustrates an acceptable method of CO control through transient inlet CO concentration and constant overall hydrogen flow rate.

The second type of transient response experiment is illustrated in Figure 11. During this experiment, a step increase in the overall flow rate was evaluated. Chemical flow rate was varied from a steady-state of 50 kWch to 100 kWch. After 90 seconds the flow reverted to the 50 kWch level. In this case, the inlet gas composition was constant including 8000 ppm CO. This type of transient replicates a system power transient. Data suggest the control strategy is dependent upon staging of air injection flow rates. A small pulse of approximately 65 ppm CO magnitude was observed if the air injection flow rates follows. the total flow rate increase. However, that perturbation was not apparent if the air injection rates were increased before the total flow rate increase. Most likely this result depends upon the flow geometry used in this apparatus. However, with appropriate control strategy, this device is capable of operating with excellent CO control through wide variation in chemical flow rate.

PROX Modeling

Development of computer models of PROX operation is an essential element in the LANL technology development Task. Although at present existing models are primarily steady state, considerable progress is evident toward the goal of developing transient PROX incorporating chemical kinetics and heat transfer. These models will support experimental analysis, design and optimization, and development of control system algorithms. Comparison of model results to experimental data will also give confidence that the chemical dynamics are adequately understood.

The steady-state computer model describing the LANL PROX concept is essentially complete.. The model describes a three-stage PROX design, but it can be easily modified to include more or less stages. Outlet gas composition from each stage is predicted based on a 1-D plug-flow reactor model built based on empirical data derived from single-stage experiments conducted previously. The model incorporates estimates of the pressure along the PROX internal passages, and describes dynamics of gas to liquid coolant heat exchange in each of the interstage gas coolers. The model has proven a useful design tool for sizing PROX components, such as the heat exchangers, for investigating operational scenarios such as variation of flow rate, inlet CO concentration, and for analysis of experimental. Figure 14 shows one result of a design-and- optimization calculation to find set point that results a hydrogen consumption minimum during cleanup. The methane production at the outlet of each PROX stage is illustrated as a function of the stage 1 oxygen stoichiometry. Figure 15 shows the model design variables for a three stage PROX operating on a 100 kWch gasoline reformate flow with 8000 ppm CO at the inlet.

Energy Partners PROX

Another PROX component is being designed, fabricated and testing to support a 10 kWe PEM fuel cell system being built by Energy Partners under Department of Energy support. This PROX design concept was derived from experience garnered using the steady-state PROX model calculations and incorporates components selected to reduce the mass of the PROX and to improve transient performance. Such components appear useful for high-volume manufacturing. The modular flanged design is retained to allow agile

PROX reconfiguration for different applications and to exchange catalysts should unanticipated poisoning occur.

Future Work

Future work will focus on the development and refinement of PROX technology to meet the requirements for PEM fuel cell systems designed for transportation applications. The existing 50 kWe PROX and experimental test facility will serve as the experimental design platform to conduct parameterization and optimization experiments that move toward verification of a transient PROX model. Partial oxidation fuel processors of different design from 1.) ADL. and 2.) Hydrogen Burner Technology will be installed for integrated fuel cell system experiments. on PROX system and performance on real versus synthetic reformate. We will continue to work with industrial partners such as Energy Partners to integrate and test LANL PROX hardware in their fuel cell systems.

A second important future focus is the definition of PROX technology for commercialization needed to meet the PNGV time schedule for fuel cell system technology for 2004 markets. This focus includes catalyst development and optimization for the automotive environment. A design-for-manufacturing exercise in partnership with Tier I suppliers begun this year will continue. LANL will work with industrial partners to them in the development of improved concepts for manufacturing engineering applied to the PROX component, including sensors, controls, and reactor design, along a pathway that leads to high performance, reliable, rugged and low cost hardware.

Los Alamos PROX: Figures

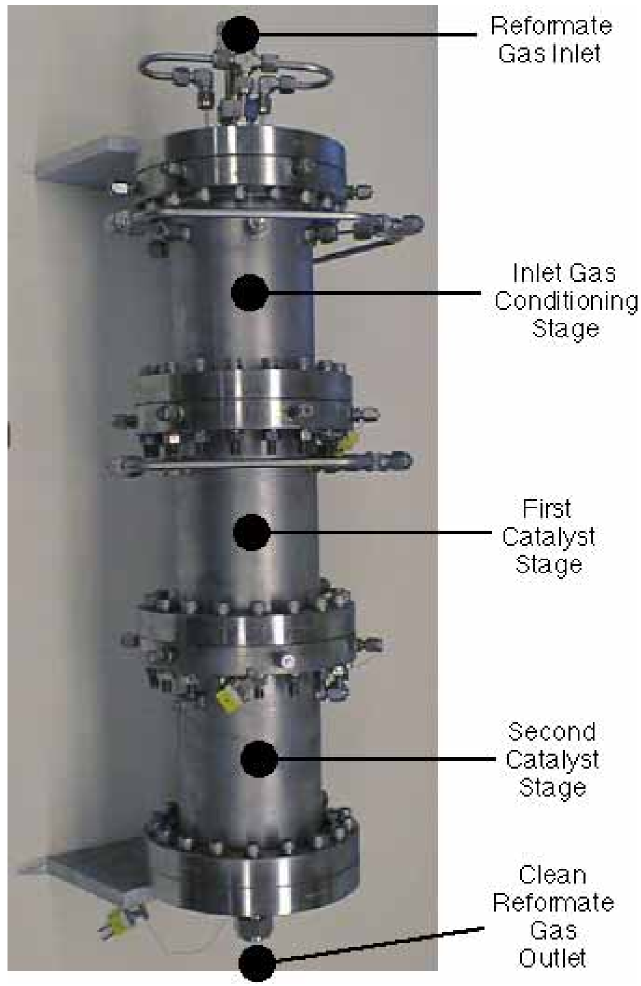

Figure 1. The modular PROX shown in this picture was used in the gasoline fuel cell system demonstration. The flanged stages allow for rapid assembly and disassembly and reconfiguration of the internal reactor including changing of the catalysts. The external tubing shown in the picture is the air injection manifold that permits multiple injection sites for each of the three stages.

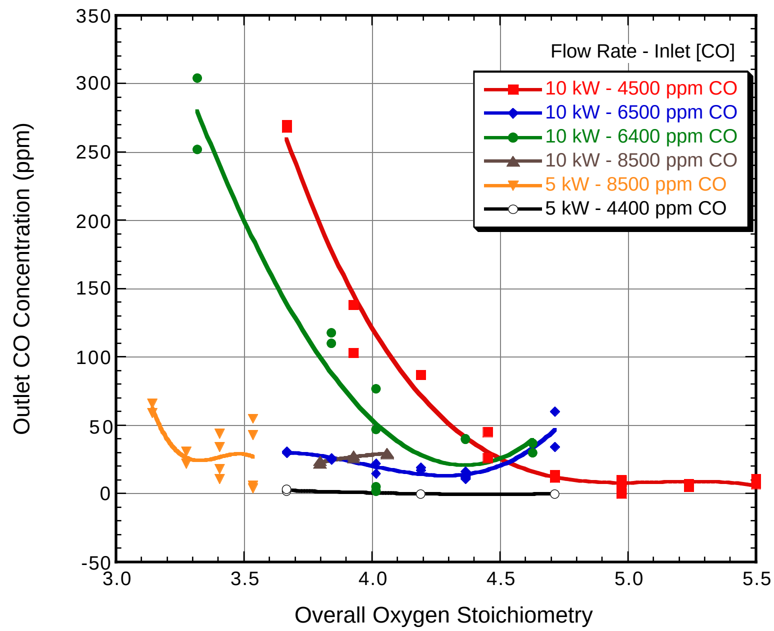

Figure 2. The measured outlet carbon monoxide concentration as a function of overall oxygen stoichiometry is shown for the modular PROX used in the gasoline system demonstration. Measurements were made at two overall simulated gasoline reformate flow rates and a range of inlet carbon monoxide concentrations.

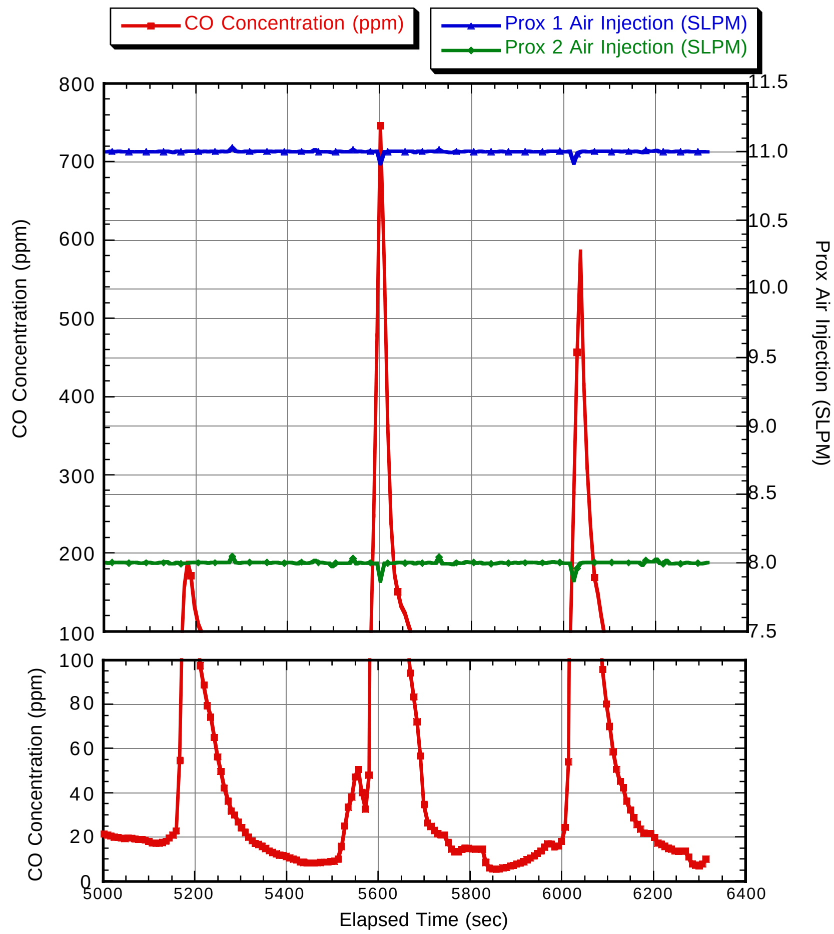

Figure 3. Outlet carbon monoxide concentration showing transient behavior from the PROX operating on gasoline reformates from the Arthur D. Little multifuel processor. PROX air injection flow rates were held constant through this time period. The range 0-100 ppm CO is expanded to show the detail of the outlet CO concentration.

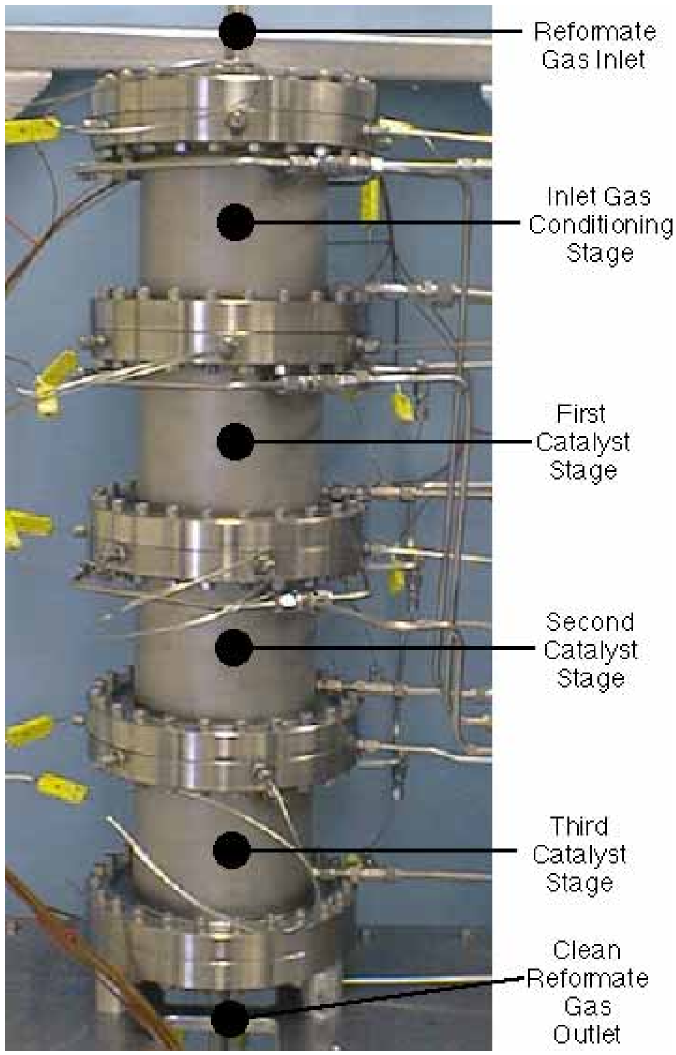

Figure 4. This picture shows the 50 kWe modular PROX assembled at the PROX test facility. The flanged stages allow for disassembly and reconfiguration of the internal reactor including changing of the catalysts. The external plumbing shown in the picture are the air injection manifolds and the coolant water inlets and outlets for each stage. Flanges (stainless steel knife edge clamped against a copper gasket) provide required hydrogen safety for the experimental laboratory facility.

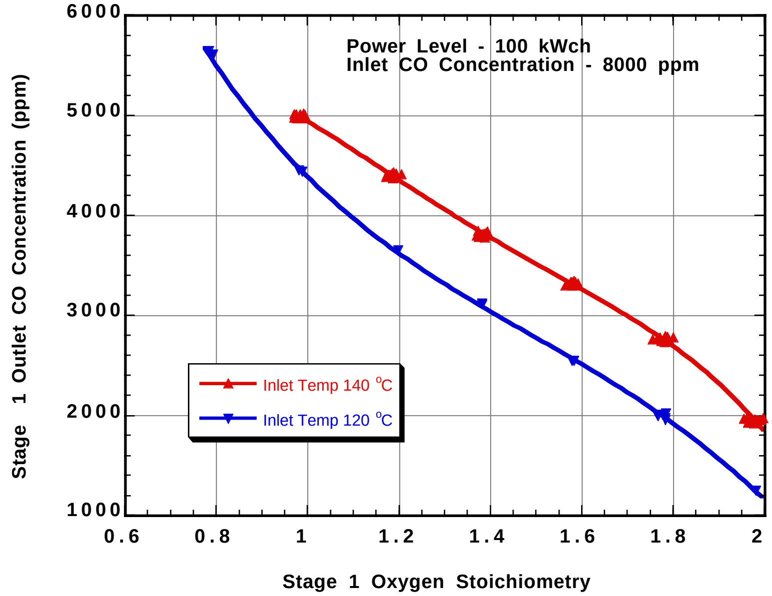

Figure 5. Outlet carbon monoxide concentrations for two inlet temperatures are shown as a function of oxygen stoichiometry for the first stage of the 50kWe PROX. The overall flow rate corresponds to 100 kWch gasoline reformate with 8000 ppm CO at the inlet.

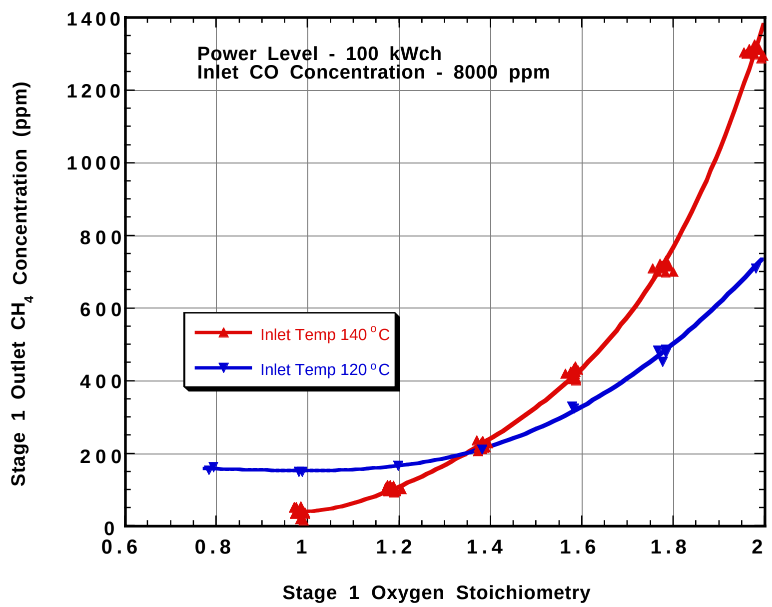

Figure 6. Outlet methane concentrations for two inlet temperatures are shown as a function of oxygen stoichiometry for the first stage of the 50kWe PROX. The overall flow rate corresponds to 100 kWch gasoline reformate with 8000 ppm CO at the inlet.

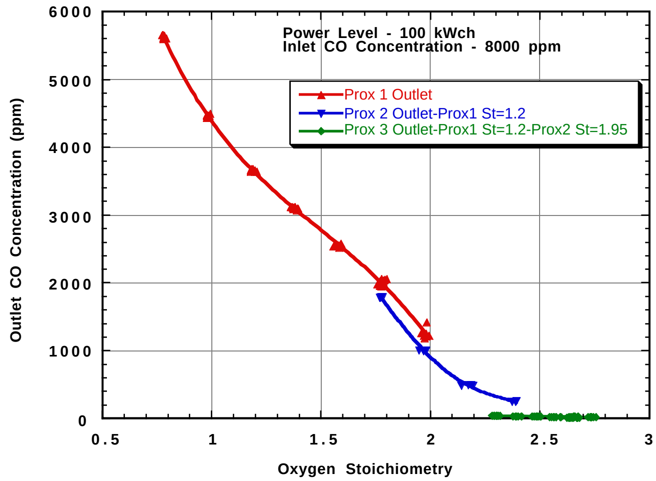

Figure 7. Outlet carbon monoxide concentrations as a function of overall oxygen stoichiometry are shown for the three stages of the 50kWe PROX. The overall flow rate corresponds to 100 kWch gasoline reformate with 8000 ppm CO at the inlet. The second stage outlet CO concentrations were measured with the first stage operating at an oxygen stoichiometry of 1.2.

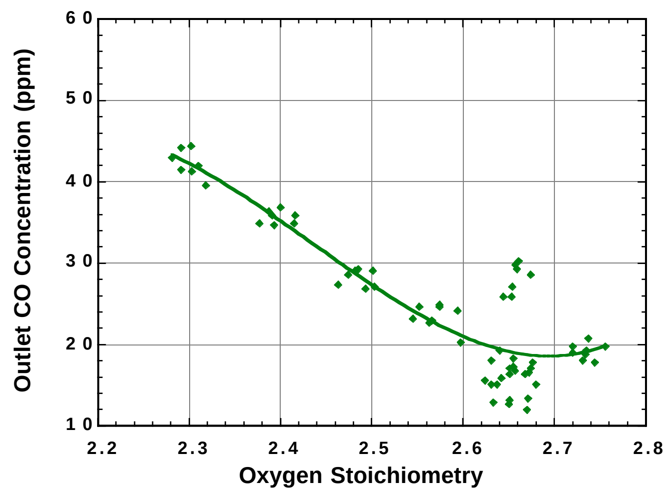

Figure 8. Outlet carbon monoxide concentrations as a function of overall oxygen stoichiometry are shown for the third stage of the 50kWe PROX. The overall flow rate corresponds to 100 kWch gasoline reformate with 8000 ppm CO at the inlet. Overall oxygen stoichiometries were 1.2 and 1.95 for the first and second stage, respectively.

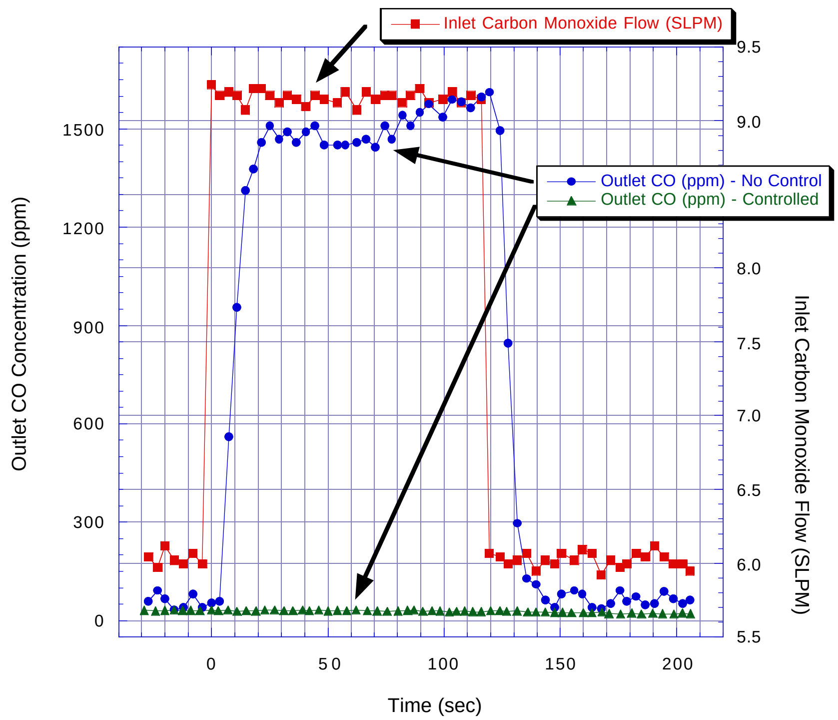

Figure 10. Outlet CO concentrations measured as a function of time for a 90 second pulsed increase in inlet CO concentration from 8000 ppm to 12000 ppm as shown by the inlet carbon monoxide flow. The overall flow rate corresponded to a 50 kWch (based on LHV of H2) synthetic gasoline reformate. Air injection flow rates were held constant for the No Control curve, while air injection flow rates were held proportional to the inlet CO flow for the Controlled curve.

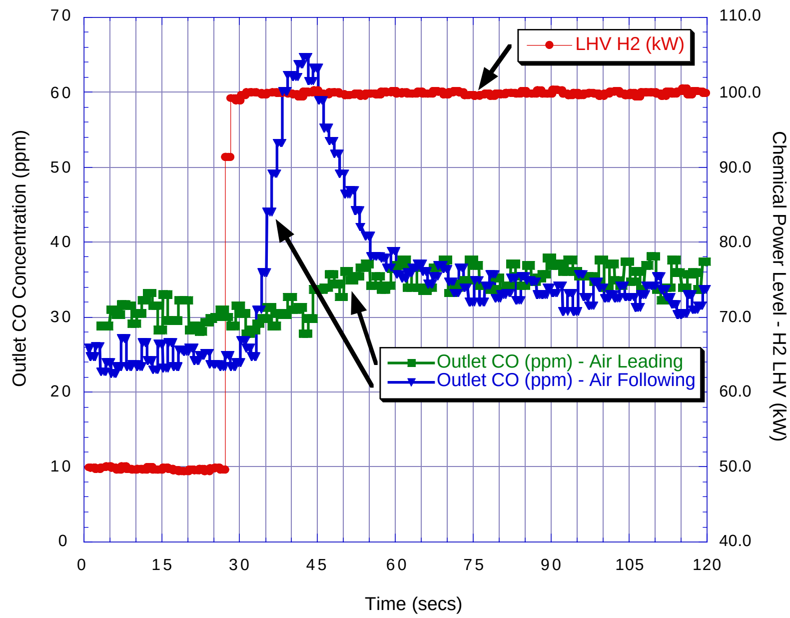

Figure 11. Outlet CO concentrations measured as a function of time for a step increase in overall flow rate from 50 kWch to 100 kWch as shown by the curve labeled LHV H2. The inlet gas composition of synthetic gasoline reformate is held constant with 8000 ppm CO.

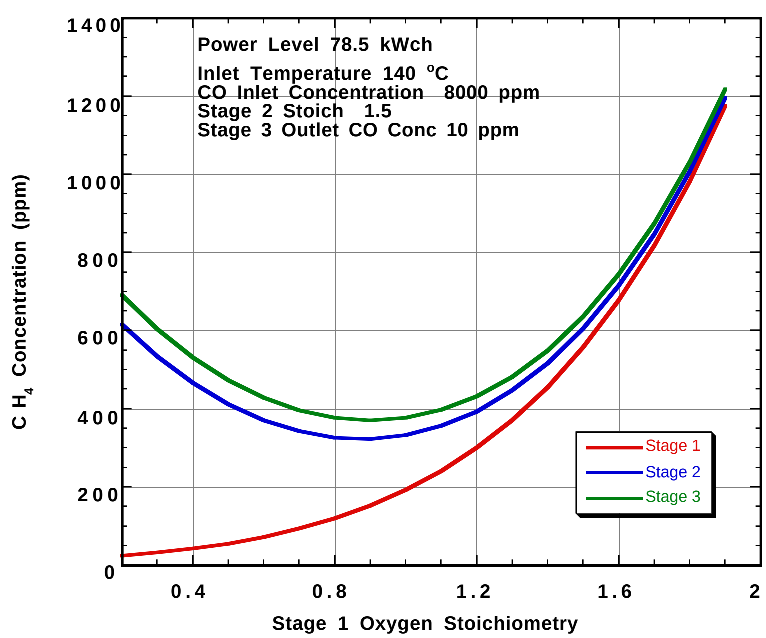

Figure 12. Outlet methane concentrations from each of the three stages of the PROX as a function of the stage 1 oxygen stoichiometry. The steady-state PROX model generated these results.

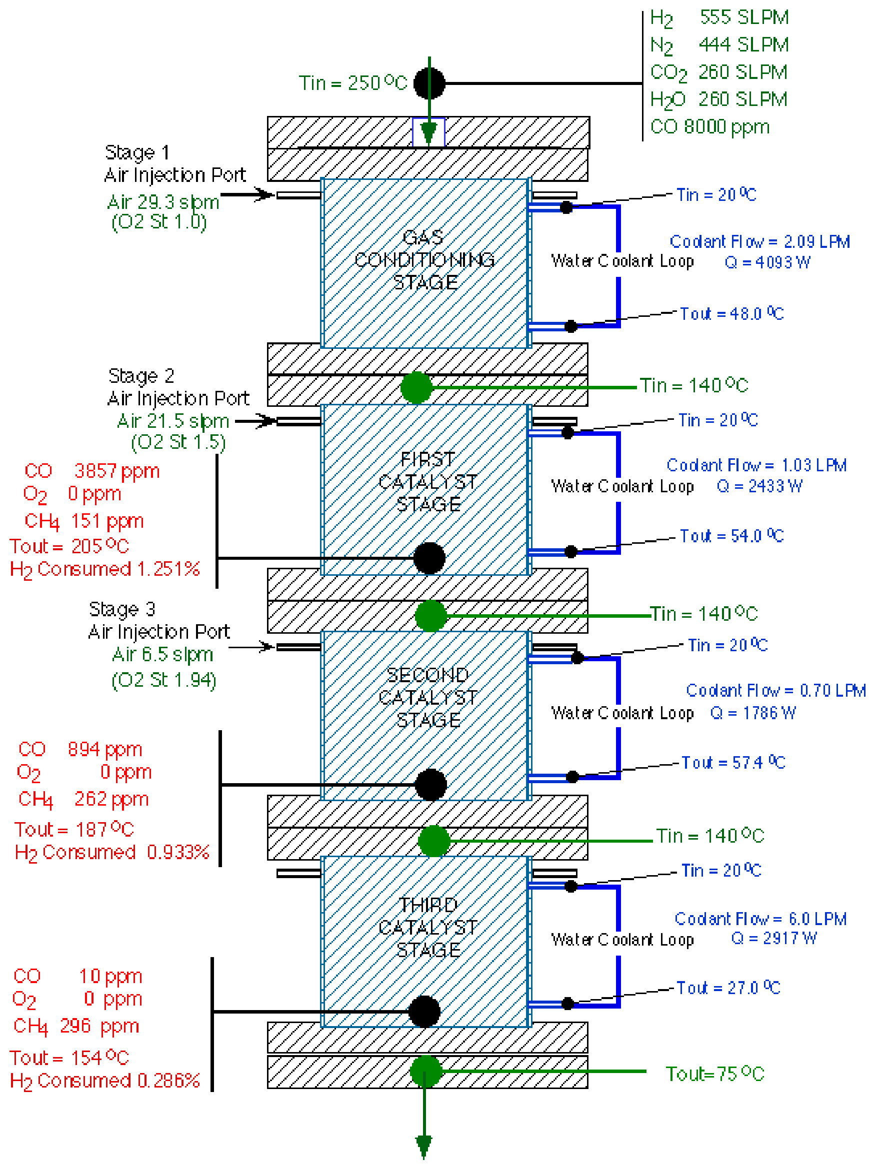

Figure 13. State points calculated by the steady-state PROX model for a 100 kWch gasoline reformate flow for one simulation selected for low hydrogen utilization.